

CLASSIFICATION

CONFIDENTIAL

CONFIDENTIAL

CENTRAL INTELLIGENCE AGENCY

REPORT

50X1-HUM

INFORMATION FROM

FOREIGN DOCUMENTS OR RADIO BROADCASTS

CD NO.

COUNTRY USSR

DATE OF INFORMATION 1940

SUBJECT Scientific - Chemistry, zirconium and tantalum

DATE DIST. 4 Jan 1951

HOW PUBLISHED Monthly periodical

WHERE PUBLISHED Moscow - Leningrad

NO. OF PAGES 6

DATE PUBLISHED Nov 1940

SUPPLEMENT TO REPORT NO.

LANGUAGE Russian

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANINGS OF ESPIONAGE ACT 80 U. S. C. 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE Zhurnal Prikladnoy Khimii, Vol XIII, No 11, 1940, pp 1545-1555.PHASE DIAGRAMS OF THE $ZrCl_4$ - $NaCl$ AND ZrO_2 - $CaCl_2$ SYSTEMS AND DIRECTIONS FOR PREPARINGPURE SALTS $ZrCl_4$ AND $TiCl_5$

N. A. Belozerskiy

O. A. Kucherenko

GIPKH (State Inst of Applied Chem)

Submitted 9 Jun 1940

[Digest. Tables and figure referred to are appended.]

Zirconium chloride belongs to the class of volatile compounds which do not melt under atmospheric pressure. Its vapor pressure reaches 760 millimeters at 331° C. It only begins to melt at 437° C at a pressure of about 25 atmospheres (1).

During electrolysis of molten sodium chloride, to which zirconium chloride had been added, pure powdered zirconium is deposited at the cathode (2). The volatility of zirconium chloride makes the choice of a suitable electrolyte for the chloride bath difficult. The total volatility of a binary system of salts is determined by the volatility of the more easily evaporated component, as long as Raoult's law applies. This will not be the case whenever formation of complex compounds takes place, and the present work was carried out in order to investigate that possibility.

When zirconium dioxide is submitted to electrolysis in molten calcium chloride, zirconium is deposited at the cathode. However, precipitation of a part of the zirconium dioxide invariably takes place at the bottom of the electrolytic bath.

- 1 -

CONFIDENTIAL

CLASSIFICATION

CONFIDENTIAL

STATE	<input checked="" type="checkbox"/> NAVY	<input checked="" type="checkbox"/> NSRB		DISTRIBUTION						
ARMY	<input checked="" type="checkbox"/> AIR	<input checked="" type="checkbox"/> FBI		<i>alc</i>	<input checked="" type="checkbox"/>					

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

Preparation of the Salts

Zircon from the Urals was used as the crude material. This mineral is a practically pure zirconium silicate containing a slight admixture of iron oxide. For the preparation of zirconium chloride, finely powdered zircon was mixed with ground charcoal in the proportion 10:4 by weight. The charge was fed into an Acheson furnace and calcined for 6-8 hours at a temperature of 2,000° C. During the process of calcination, the bulk of silicon and iron is sublimed. The product is a fused or crystalline mixture of zirconium carbides containing a small quantity of iron and probably some carborundum. This product was either chlorinated as it came from the Acheson furnace or else upon grinding and briquetting with charcoal in the proportion of 10:3. Chlorination was carried out at 600-650° C in a nichrome tubular furnace. This method has been described before (3).

[In reference 3, the preparation of pure tantalum pentachloride is described. The crude material is the so-called technical oxide of columbium which contains approximately 50% of the combined oxides of columbium and tantalum, about the same quantity of titanium oxide, and 1-2% of iron oxide. The proportion of tantalum oxides to columbium oxides fluctuates between 1:8 and 1:16. The technical oxide (one kg) was briquetted with charcoal (300 grams), using molasses as a binder. The briquettes were dried at 70-90° C and coked at 750-800° C.

The coked briquettes prepared according to this procedure were chlorinated at 650-700° C. The furnace for chlorinating consisted of a vertical quartz tube one meter long which had an inner diameter of 80 millimeters and was equipped with a nichrome heater. Chlorine dried in Tishchenko flasks filled with sulfuric acid was supplied from the top while the volatile chlorides were distilled out through the bottom outlet. These chlorides were partly captured in two iron receptacles connected to the bottom outlet in series and having capacities of 20 and 15 liters. These receptacles were heated to 140-150° C by means of burners to remove as completely as possible titanium chloride.

The mixture of chlorides and oxychlorides of columbium and tantalum obtained in this manner contained, besides compounds of these two metals, about 1-2% of titanium chlorides and 2-5% of iron chlorides. This mixture was reduced with sodium according to the procedure described by N. A. Belozerskiy, K. I. Rezvaya, and B. A. Freydina in GIPKh report No 96 -37 (2). The resulting metal powder was first washed with water to remove sodium chloride and then with dilute hydrochloric acid to remove iron.

For the preparation of pure chlorides of columbium and tantalum, a second chlorination was carried out. To prevent contamination with oxygen, the chlorine from the cylinder, after being dried with sulfuric acid and phosphorus pentoxide, was conducted through a tubular furnace of the type described above. This furnace, which operated in a horizontal position, was filled with incandescent charcoal which eliminated all the oxygen contained in the chlorine. The chlorination took place in a second horizontal tubular furnace following the one filled with charcoal. The chlorides were collected in a special receptacle (consisting of two bulbs and equipped with a Bunsen valve at the end removed from the furnace). This receptacle was heated in order to drive off the titanium chloride.

The mixture of chlorides of columbium and tantalum was dissolved in water. On precipitation with ammonia, the oxides were dissolved in hydrofluoric acid in a platinum dish. On addition of potassium fluoride, potassium fluorotantalate precipitated. The latter was freed of traces of columbium by repeated recrystallization from water containing hydrogen fluoride. The fluorotantalate which had been purified by recrystallization was filtered and dried

- 2 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

on platinum dishes. Thereupon the salt was reduced to tantalum with sodium and the metallic tantalum chlorinated in the same manner as the mixture of columbium and tantalum in the second chlorination. The mixture of tantalum chloride and tantalum oxichloride was separated by distillation in a stream of chlorine.

The zirconium chloride which was collected in the receptacle following the chlorination furnace contained admixtures of iron chloride and zirconium oxychloride. Silicon chloride did not remain in the receptacle. The zirconium chloride was mixed with an equal weight of sodium chloride and stoichiometric quantity of sodium metal. On heating this mixture under proper conditions (2), the zirconium was reduced to a metal powder. This powder was washed with hydrochloric acid in order to remove iron.

The purified metal powder was used for the preparation of zirconium chloride. All precautions were taken (by eliminating water and oxygen, especially from the chlorine) to avoid the formation of zirconium oxychloride (3) [see excerpt from reference 3 above]. Before chlorination was started, all air was displaced from the apparatus with chlorine. The zirconium chloride was collected in a graduate or the special receptacle described in reference (3). Notwithstanding the precautions, the resulting chloride, besides traces of iron, contained oxychloride. To get rid of the oxychloride, the product had to be distilled twice.

Technique of Measurements

By reason of the high volatility of zirconium chloride and the tendency toward hydrolysis exhibited by both zirconium chloride and calcium chloride, the data for the phase diagrams had to be determined in hermetically sealed vessels and in the medium of a suitable gas, namely chlorine. Depending on the solidification temperature, either a quartz or a pyrex vessel had to be used. The test-tube-shaped vessels were equipped with ground stoppers through which a slender U-tube made of quartz or pyrex glass reached almost to the bottom of the vessel. The U-tube served as a sheath for the thermocouple. In the case of volatile mixtures, the vessel had two side arms equipped with valves. Zirconium chloride was distilled into the vessel through these arms in a stream of chlorine. When the volatility was low enough, a similar vessel lacking these arms was used.

The precision of the measurements was no higher than $\pm 5^{\circ}\text{C}$.

The mixture was prepared in the following manner: First the vessel was filled with chlorine. Under a current of chlorine, sodium chloride was added, whereupon zirconium chloride ((in a powdered form) was rapidly poured in or else distilled in from the furnace or zirconium chloride receptacle. In the case of $\text{ZrO}_2 - \text{CaCl}_2$, anhydrous calcium chloride was fused in the vessel in a current of chlorine. Bubbling of chlorine through the molten calcium chloride was continued for 1-2 hours. Then zirconium oxide was added and the bubbling of gas stopped.

Heating and cooling were carried out in a crucible furnace. The temperature was measured every 30 seconds.

$\text{ZrCl}_4 - \text{NaCl}$ System

The results of the measurements are shown in Figure 1 and Table 1. The samples were analyzed on completion of the experiments.

In view of the high volatility of zirconium chloride, the experimental investigation was limited to samples containing less than 90% of zirconium chloride by weight. This covers all mixtures which are of practical value. Attempts to

- 3 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

carry out determinations in sealed tubes on mixtures containing more than 90% of zirconium chloride failed, because the high vapor pressure which developed at the temperature of melting resulted in the bursting of tubes.

The phase diagram shows two definite compounds corresponding to 4 NaCl . ZrCl_4 and $\text{NaCl} \cdot \text{ZrCl}_4$. There is also the possibility that the unstable compound $2 \text{ NaCl} \cdot \text{ZrCl}_4$ exists. The melting points of the three eutectics are 390°C , 220°C , and 162°C . The melting points of the two well defined compounds are 535°C and 330°C .

$\text{ZrO}_2 - \text{CaCl}_2$ System

As can be seen from the results given in Table 2, the phase diagram of the $\text{ZrO}_2 - \text{CaCl}_2$ system discloses a total lack of solubility. This finding is rather puzzling, because it has been established that zirconium is deposited on a copper cathode from the melt in question (2).

Two explanations of this fact are possible. First, a discharge of zirconium ions originating from genuinely dissolved zirconium dioxide may occur, although the quantity in solution is too small to produce a measurable depression of the melting point. In this case, the equilibrium disturbed by electrolysis is re-established by subsequent solution of additional zirconium dioxide at a rate which is precisely equal to the rate of electrolytic decomposition. Another possibility would be that metallic calcium is deposited and that it immediately reacts with suspended particles of zirconium dioxide, reducing the latter compound to metallic zirconium.

The results obtained in this instance do not preclude the possibility that zirconium dioxide may be soluble in calcium chloride at other, possibly higher, temperatures.

BIBLIOGRAPHY

1. Rahlfs and Fischer, Z. Anorg. Chemie, Vol. CCXI, p. 351, 1933; Z. Elektrochem., Vol XXXVIII, p 592, 1932.
2. N. A. Belozerskiy, K. I. Rezvaya, and B. A. Freydina, GIPKh Report No 96-37.
3. N. A. Belozerskiy and K. I. Rezvaya, Zhurnal Prikladnoy Khimii, Vol XIII, p 1545-1551.

[Tables and figure on following pages]

- 4 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

Table 1. ZrCl_4 - NaCl System

Comp of salt According to Analysis				Temp Arrests		Remarks
Wt (%)		Mol (%)		I	II	
ZrCl ₄	NaCl	ZrCl ₄	NaCl			
0	100	0	100	800		The sample for analysis was taken at the end of the experiment. The analytical methods are described in GIPKh Report No 96-37.
8.7	91.3	2.2	97.8	680	408	
10.4	89.6	2.6	97.4	603	380	
13.2	86.8	3.2	96.8	560	390	
22.3	77.7	6.2	93.8	515	405	
22.8	77.2	6.4	93.6	--	395	
22.8	77.2	6.4	93.6	515	380	
27.0	73.0	8.2	91.8	480	390	
28.3	71.7	8.8	91.2	465	388	
35.4	64.6	12.2	87.8	423	395	
37.3	62.7	13.3	86.7	460	372	
37.6	62.4	13.4	86.6	488	400	
42.2	57.8	15.8	84.2	525	380	
47.8	52.2	19.0	81.0	535	390	
50.9	49.1	20.8	79.2	530	390	
56.3	43.7	24.5	75.5	500	--	
57.1	42.9	25.0	75.0	470	395	
57.7	42.3	25.7	74.3	480	406	
58.9	41.1	26.6	73.4	400	--	
62.3	37.7	29.5	70.5	395	--	
70.0	30.0	37.0	63.0	270	220	
72.0	28.0	39.0	61.0	250	220	
74.6	25.4	42.0	58.0	217	--	
76.8	23.2	44.8	55.2	307	--	

- 5 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

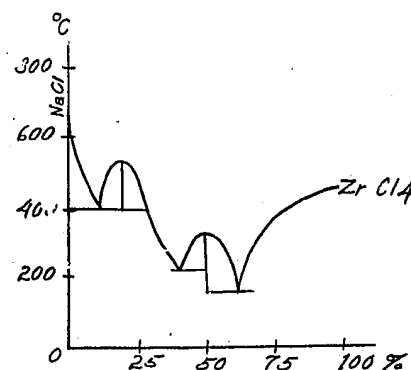
50X1-HUM

Table 1. (Contd)

Comp of salt According to Analysis		Temp Arrests		Remarks	
Wt (%)		Mol (%)			
<u>ZrCl₄</u>	<u>NaCl</u>	<u>ZrCl₄</u>	<u>NaCl</u>	<u>I</u>	<u>II</u>
77.0	23.0	45.2	54.8	305	220
80.0	20.0	50.0	50.0	330	230
86.2	13.8	60.4	39.6	217	167
87.6	12.4	64.0	36.0	212	162
88.8	11.2	66.0	34.0	262	160

Table 2. ZrO₂ - CaCl₂ System

Comp of Salt in Wt (%)		Comp of Salt in Mol (%)		Pt of Arrest
<u>ZrO₂</u>	<u>CaCl₂</u>	<u>ZrO₂</u>	<u>CaCl₂</u>	<u>Temp (° C)</u>
0	100	0	100	770
5	95	4.52	95.48	772
6.2	93.8	5.62	94.38	771
12.8	87.2	11.70	88.30	767

Figure 1. Composition - Melting Point Diagram of the ZrCl₄ - NaCl System

- E N D -

- 6 -

CONFIDENTIAL

CONFIDENTIAL